

## CONFIRMATION OF CIRCUMSTELLAR PHOSPHINE

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## ABSTRACT

Phosphine (PH<sub>3</sub>) was tentatively identified a few years ago in the carbon star envelopes IRC +10216 and CRL 2688 from observations of an emission line at 266.9 GHz attributable to the  $J = 1 - 0$  rotational transition. We report the detection of the  $J = 2 - 1$  rotational transition of PH<sub>3</sub> in IRC +10216 using the HIFI instrument on board *Herschel*, which definitively confirms the identification of PH<sub>3</sub>. Radiative transfer calculations indicate that infrared pumping to excited vibrational states plays an important role in the excitation of PH<sub>3</sub> in the envelope of IRC +10216, and that the observed lines are consistent with phosphine being formed anywhere between the star and 100  $R_*$  from the star, with an abundance of  $10^{-8}$  relative to H<sub>2</sub>. The detection of PH<sub>3</sub> challenges chemical models, none of which offers a satisfactory formation scenario. Although PH<sub>3</sub> locks just 2 % of the total available phosphorus in IRC +10216, it is together with HCP, one of the major gas phase carriers of phosphorus in the inner circumstellar layers, suggesting that it could be also an important phosphorus species in other astronomical environments. This is the first unambiguous detection of PH<sub>3</sub> outside the solar system, and a further step towards a better understanding of the chemistry of phosphorus in space.

*Subject headings:* astrochemistry — line: identification — molecular processes — stars: AGB and post-AGB — circumstellar matter — stars: individual (IRC +10216)

## 1. INTRODUCTION

Phosphorus being a biogenic element, the study of the various forms in which it is present in the different astronomical environments is a matter of great interest, although still poorly understood (Maciá 2005). Only five P-containing molecules (PN, CP, HCP, PO, and C<sub>2</sub>P) have been observed in the gas phase of interstellar and circumstellar media (Turner & Bally 1987; Ziurys 1987; Guélin et al. 1990; Agúndez et al. 2007; Tenenbaum et al. 2007; Halfen et al. 2008). These five molecules are all observed in circumstellar envelopes around evolved stars. However, in interstellar clouds only PN is observed and with a relatively low abundance, implying that most of phosphorus must be elsewhere, probably depleted in dust grains (Turner et al. 1990).

Phosphine (PH<sub>3</sub>), the phosphorus cousin of ammonia, is a relatively stable molecule that could be locking an important fraction of phosphorus in various astronomical environments. Since more than 30 years ago, PH<sub>3</sub> is known to be present in the atmospheres of the giant gaseous planets Jupiter and Saturn, where it is the major phosphorus carrier (Bregman et al. 1975; Larson et al. 1977; Weisstein & Serabyn 1996). Upper limits obtained in Neptune and Uranus imply that the gas phase abundance of phosphorus is probably subsolar in the atmosphere of these icy giants (Moreno et al. 2009). Phosphine ice is also a plausible major phosphorus constituent

of comets, although recent searches in the gaseous coma of a few comets turned out unsuccessful, providing upper limits not significant enough to conclude whether or not PH<sub>3</sub> locks most of phosphorus in these solar system bodies (Crovisier et al. 2004; Agúndez et al. 2014).

Outside the solar system, no evidence has been found about the presence of PH<sub>3</sub> in interstellar clouds, either in the gas phase or as ice in dust grains. There is however some evidence of PH<sub>3</sub> being present in the outflows of evolved stars. A few years ago this molecule was tentatively identified in the carbon star envelope IRC +10216. The identification was based on the  $J = 1 - 0$  rotational transition, lying at 266.9 GHz, which however appeared contaminated by a narrow line assigned to SiS in its  $v = 4$  vibrational state (Agúndez et al. 2008). An emission feature attributable to the  $J = 1 - 0$  line of PH<sub>3</sub> was also observed independently by Tenenbaum et al. (2008) in the spectra of IRC +10216 and the carbon-rich envelope CRL 2688. The observation of just one line, affected by blending in the case of IRC +10216, led to consider the detection of PH<sub>3</sub> as tentative. Here we report the detection of the  $J = 2 - 1$  rotational transition of PH<sub>3</sub> in IRC +10216 using the HIFI instrument on board *Herschel*, which definitively confirms the identification of phosphine in this source. This is the first time that PH<sub>3</sub> is unambiguously observed outside the solar system.

2. OBSERVATIONS: IDENTIFICATION OF PH<sub>3</sub>

The HIFI observations of IRC +10216 were obtained in May and from October to December 2010, in the context of two GT1 programmes dedicated to perform a line survey in all HIFI bands and to search for light hydrides at selected frequencies. Data were taken in double beam-switching mode with a spectral resolution of 1.1 MHz and a channel spacing of 0.5 MHz, and processed using the standard *Herschel* pipeline up to level 2, which provides fully calibrated spectra in the antenna temperature scale. The intensity scale was later on transformed

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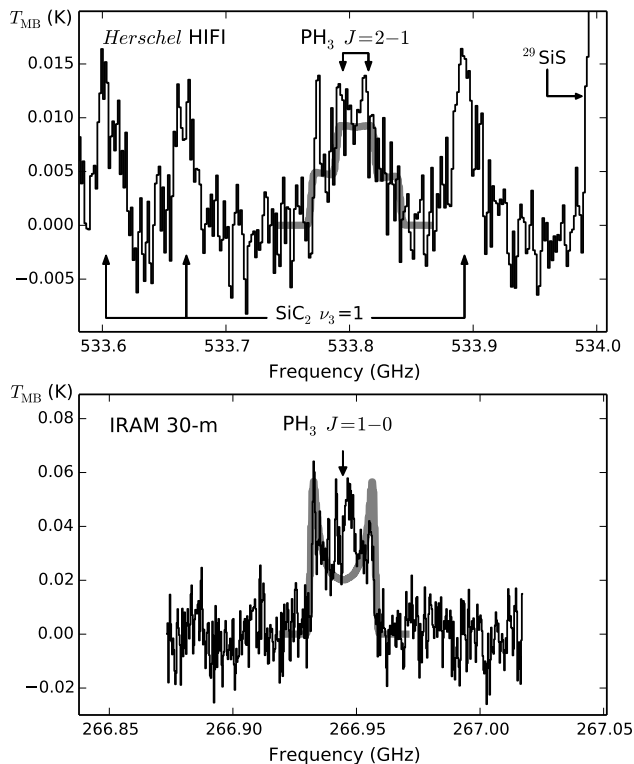


FIG. 1.—  $\text{PH}_3$  lines observed in IRC +10216 (black histogram). The lower panel shows the  $J = 1 - 0$  transition at 266.9 GHz observed with the IRAM 30-m telescope at a spectral resolution of 0.32 MHz. An overlapping narrow line arising from  $\text{SiS } v = 4$  has been subtracted (see Agúndez et al. 2008). The upper panel shows the  $J = 2 - 1$  transition (consisting of  $K = 0$  and  $K = 1$  components) at 533.8 GHz observed with *Herschel* HIFI. The spectrum, smoothed to a spectral resolution of 1.5 MHz, shows also three lines of  $\text{SiC}_2 \nu_3 = 1$  and one line of  $^{29}\text{SiS}$ . Thick gray lines are the line profiles calculated with the LVG model (see section 3). The central peak observed in the  $J = 1 - 0$  line, not accounted for by the model, is probably due to a non optimal subtraction of the  $\text{SiS } v = 4$  overlapping line.

to main beam brightness temperature  $T_{\text{MB}}$ . The local oscillator was shifted in frequency to identify any emission arising from the image band. Spectra were smoothed to a spectral resolution of 1.5 MHz. For details about the data reduction we refer to Cernicharo et al. (2010).

Phosphine was searched for in IRC +10216 with HIFI through its  $J = 2 - 1$  and  $J = 3 - 2$  rotational transitions. This molecule is an oblate symmetric rotor and thus its rotational levels are defined by the quantum numbers  $J$  and  $K$ , and radiative transitions are only allowed within levels of the same  $K$  ladder. The  $K$  ladders are grouped into two distinct forms: ortho and para, between which radiative and collisional transitions are severely forbidden. The rotational spectrum of  $\text{PH}_3$  has been extensively studied in the laboratory and line frequencies are accurately known (Cazzoli & Puzzarini 2006; Müller 2013; Sousa-Silva et al. 2013). Its electric dipole moment has been measured as 0.574 D (Davies et al. 1971).

The  $J = 2 - 1$  rotational transition of  $\text{PH}_3$  consists of two  $K$  components:  $2_0 - 1_0$  at 533.7946 GHz and  $2_1 - 1_1$  at 533.8153 GHz. The HIFI spectrum of IRC +10216 at these frequencies is shown in the upper panel of Fig. 1. The  $T_{\text{MB}}$  rms noise level is 0.0024 K per 1.5 MHz channel. There is an emission feature with  $T_{\text{MB}} \sim 0.01$  K cen-

tered at 533.8 GHz which can be clearly identified with a composite of the two  $K$  components of the  $J = 2 - 1$  transition of  $\text{PH}_3$ . We have verified that there is no other obvious assignment for this emission feature by looking at the spectral catalog of MADEX (Cernicharo 2012). Each of the two  $K$  components has a linewidth consistent with an expansion velocity  $v_{\text{exp}}$  of  $14.5 \text{ km s}^{-1}$ , as most of lines arising from the outer envelope in IRC +10216 (Cernicharo et al. 2000), including the line previously observed with the IRAM 30-m telescope and assigned to the  $J = 1 - 0$  transition of  $\text{PH}_3$  (see lower panel of Fig. 1 and Agúndez et al. 2008). The spectrum around 533.8 GHz also shows three narrow lines, with  $v_{\text{exp}} \sim 8\text{--}10 \text{ km s}^{-1}$ , arising from  $\text{SiC}_2$  in its  $\nu_3 = 1$  vibrational state and one from  $^{29}\text{SiS}$ . Lines from these species have been already observed in IRC +10216 at millimeter wavelengths (Cernicharo et al. 2000; Agúndez et al. 2012) and are also detected across the HIFI spectral scan.

The  $J = 3 - 2$  transition of  $\text{PH}_3$  lying at 800.5 GHz is not detected because the sensitivity of the HIFI spectrum at these frequencies is not good enough. The  $T_{\text{MB}}$  rms noise level is 20 mK per 1.5 MHz channel and this  $\text{PH}_3$  line is expected to have a  $T_{\text{MB}}$  of some mK. Moreover, even if the sensitivity were much better, the detection of this line would be hampered by the fact that the  $K = 0$  and  $K = 1$  components, at 800.4562 GHz and 800.4871 GHz, would appear severely blended with two strong lines from  $\text{SiC}_2$  ( $34_{10,25}\text{--}33_{10,24}$  and  $34_{10,24}\text{--}33_{10,23}$  at 800.4842 GHz and 800.4907 GHz; Müller et al. 2012). Intense lines from warm  $\text{SiC}_2$  are numerous across the whole HIFI spectrum (Cernicharo et al. 2010). The  $K = 2$  component of  $\text{PH}_3$ , at 800.5799 GHz, does not overlap with these  $\text{SiC}_2$  lines (linewidths in IRC +10216's spectra at these frequencies are  $\sim 80$  MHz) and thus would be observable if the sensitivity were good enough.

The detection of the  $J = 2 - 1$  transition of  $\text{PH}_3$  with HIFI, together with the previous detection of the  $J = 1 - 0$  line (Agúndez et al. 2008; Tenenbaum et al. 2008), definitively confirms the identification of  $\text{PH}_3$  in IRC +10216. The non detection of the  $J = 3 - 2$  line in our HIFI data is consistent with the line intensities of the  $J = 1 - 0$  and  $J = 2 - 1$  lines, and thus with the identification of  $\text{PH}_3$ .

### 3. DISCUSSION

To extract information about the abundance, spatial distribution, and excitation of  $\text{PH}_3$  in the envelope of IRC +10216 the observed lines must be confronted with the results of excitation and radiative transfer calculations. Here the calculations are based on a multi-shell LVG formalism and the model of the envelope adopted is that of Agúndez et al. (2012). Basically, it consists of an AGB star surrounded by a spherically expanding envelope of gas and dust. The adopted distance and mass loss rate are 130 pc and  $2 \times 10^{-5} M_{\odot} \text{ yr}^{-1}$ , and dust is assumed to condense at a radius of  $5 R_*$ . The stellar properties, radial profiles, and dust parameters are described in Agúndez et al. (2012). In the innermost layers ( $< 5 R_*$ ), we have adopted the downward revision of the density of particles derived by Cernicharo et al. (2013) from ALMA observations of HNC in various excited vibrational states.

Energy levels and transition frequencies of  $\text{PH}_3$  in its ground vibrational state were computed from the rota-

tional constants reported by Cazzoli & Puzzarini (2006). Line strengths for pure rotational transitions were computed from the dipole moment measured by Davies et al. (1971). Both ortho and para forms of PH<sub>3</sub> were considered with the statistical ortho-to-para ratio of 1. Since rate coefficients for collisional excitation of PH<sub>3</sub> with H<sub>2</sub> or He are not known, we adopted those computed for NH<sub>3</sub> (Danby et al. 1988; Machin & Roueff 2005), properly corrected to the case without inversion doubling. Scaling of the rate coefficients due to the mass change from NH<sub>3</sub> to PH<sub>3</sub> is very small (<5 %) and was thus not considered. No extrapolation in temperature was done, and thus the rate coefficients at 300 K, the highest temperature available in the quantum calculations of NH<sub>3</sub>, were adopted at higher temperatures. The use of these rate coefficients is probably the major source of uncertainty introduced in the excitation calculations. We included rotational levels up to  $J_K = 7_6$  for the ortho species and  $J_K = 5_5$  for para PH<sub>3</sub>, the highest levels involved in the quantum calculations of the collisional rate coefficients for NH<sub>3</sub>. Infrared pumping to excited vibrational states was taken into account by including the first excited states of the four vibrational modes  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ , and  $\nu_4$ , lying at 2321, 992, 2327, and 1118 cm<sup>-1</sup>, respectively, over the ground state. Spectroscopic constants and band intensities were taken from laboratory measurements (Baldacci et al. 1980; Tarrago et al. 1984; Fusina & Di Lonardo 2000; Brown et al. 2002; Yurchenko et al. 2006; Sousa-Silva et al. 2013). The fundamental bands of these modes lie at 4.3, 9, and 10  $\mu$ m, wavelengths at which the flux in the envelope of IRC +10216 is large (Cernicharo et al. 1999). Collisional rates for ro-vibrational transitions were assumed to be negligible compared with radiative rates.

The spatial distribution of phosphine in the envelope of IRC +10216 is uncertain because the observed line profiles provide just limited information. In the case of the  $J = 1 - 0$  line, the subtraction of the blended line of SiS  $v = 4$  introduces an important uncertainty on the real shape of the PH<sub>3</sub> contribution. The profile of the  $J = 2 - 1$  line is complicated by the overlap of the  $K = 0$  and  $K = 1$  components and the limited signal-to-noise ratio. In any case, the PH<sub>3</sub> lines observed show a width consistent with an expansion velocity of 14.5 km s<sup>-1</sup>, which indicates that an important part of the PH<sub>3</sub> emission comes from regions where the gas has already reached the terminal expansion velocity of the envelope. Whether phosphine is formed close to the star or farther out in the envelope is unknown, although there are reasons to suspect that it is not formed too close to the star. On the one hand the abundance of PH<sub>3</sub> predicted at thermochemical equilibrium in the hot and dense surroundings of the star is negligible, <10<sup>-12</sup> relative to H<sub>2</sub> (Agúndez et al. 2007). On the other, infrared observations rule out the presence of an important amount of the related molecule NH<sub>3</sub> inside a radius of  $\sim 20 R_*$  (Keady & Ridgway 1993; Monnier et al. 2000). Following Hasegawa et al. (2006) and Agúndez et al. (2008) here we assume that PH<sub>3</sub> is formed at an inner radius of  $20 R_*$ . The outer boundary is calculated with a photochemical model in which PH<sub>3</sub> is photodissociated by the external UV field using the rate guessed by MacKay & Charnley (2001). We find that to reproduce the observed lines (see

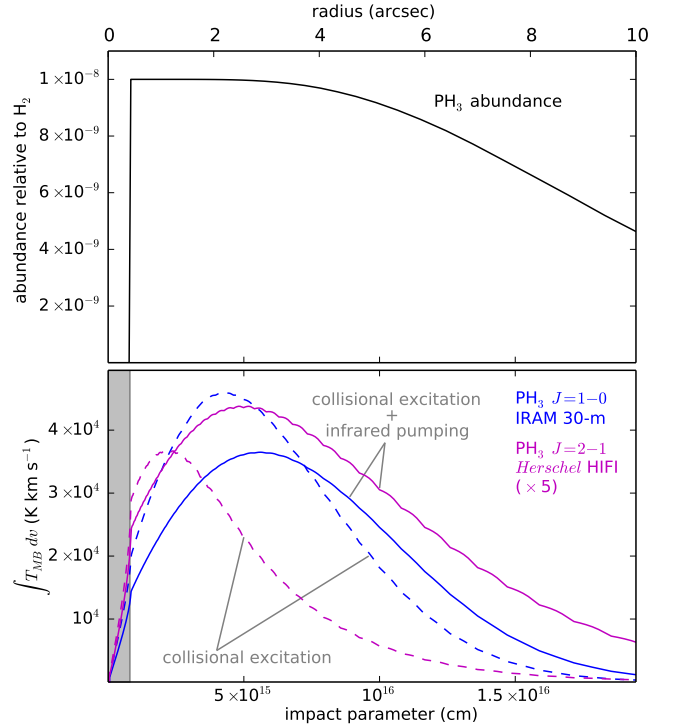


FIG. 2.— Upper panel: fractional abundance radial profile adopted for PH<sub>3</sub>. Phosphine is assumed to be present from  $20 R_*$  with an abundance of  $10^{-8}$  relative to H<sub>2</sub> and to decrease in the outer layers due to photodissociation by interstellar UV photons. Lower panel: velocity-integrated intensity computed as a function of the impact parameter for the  $J = 1 - 0$  and  $J = 2 - 1$  lines of PH<sub>3</sub>. The integration over impact parameter (if expressed as angular distance in radians) of the magnitude plotted in the ordinate axis yields the calculated value of  $\int T_{MB} dv$ . The shaded area corresponds to the region inner to  $20 R_*$ . The two panels share a common abscissa axis.

Fig. 1) we need a PH<sub>3</sub> abundance of  $10^{-8}$  relative to H<sub>2</sub>, which is just slightly higher than the value previously derived by Agúndez et al. (2008) from the  $J = 1 - 0$  line. The adopted abundance profile is shown in the upper panel of Fig. 2.

Various conclusions can be drawn from a careful inspection to the excitation and radiative transfer calculations. The first is that infrared pumping to excited vibrational states plays an important role in the excitation of PH<sub>3</sub> in the envelope. It increases the excitation temperature of rotational transitions within the ground vibrational state, and therefore their line intensities, especially the  $J = 2 - 1$  and higher  $J$  transitions, and extends the emitting region of the lines to larger radii. This can be appreciated in the lower panel of Fig. 2, where we show the contribution to the velocity-integrated line intensity of rays arising at each impact parameter. It can be seen that the bulk of the emission in the  $J = 1 - 0$  and  $J = 2 - 1$  lines comes from regions with impact parameters from the star between  $1''$  and  $6''$ . That is, the emission size of the  $J = 1 - 0$  line is of the order of the main beam of the IRAM 30-m telescope ( $9.2''$  at 266.9 GHz) while the  $J = 2 - 1$  line is highly diluted in the main beam of HIFI ( $40''$  at 533.8 GHz). We can also appreciate that the observed lines of PH<sub>3</sub> do not trace the regions inner to  $20 R_*$ . Even if we extended phosphine down to the stellar photosphere, the contribution of impact pa-

rameters shorter than  $20 R_*$  to the velocity-integrated line intensities would be less than 5 %. In fact, our LVG calculations indicate that the observed lines are compatible with  $\text{PH}_3$  being formed anywhere between the stellar surface and  $\sim 100 R_*$ .

Assuming that the elemental abundance of phosphorus in IRC +10216 is solar ( $\text{P}/\text{H} = 2.6 \times 10^{-7}$ ; Asplund et al. 2009), it turns out that HCP locks 5 % of phosphorus (Agúndez et al. 2007, 2012) while  $\text{PH}_3$  takes 2 %. It is likely that the rest of P is in some condensed form taking part of dust grains. In envelopes around other evolved stars gas phase molecules seem to lock a greater fraction of phosphorus than in IRC +10216. Around half of P is in the form of HCP and  $\text{PH}_3$  in the carbon-rich envelope CRL 2688 (Milam et al. 2008; Tenenbaum et al. 2008), while in oxygen-rich objects PO and PN contain a good fraction of the available P, around 1/4 in VY CMa (Tenenbaum et al. 2007; Milam et al. 2008) and essentially all available phosphorus in IK Tau (De Beck et al. 2013).

In IRC +10216 phosphine is formed somewhere between 1 and  $100 R_*$  from the star, although it is not clear which is the main formation mechanism. Thermochemical equilibrium calculations indicate that its abundance in the surroundings of the star is very low ( $< 10^{-12}$  relative to  $\text{H}_2$ ) and gas phase chemical kinetics models yield no net formation in the outer layers of the envelope (Agúndez et al. 2007). There are various plausible non-equilibrium processes at work in the inner envelope, which may be at the origin of  $\text{PH}_3$  and other hydrides such as  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , for which thermochemical equilibrium predicts abundances much lower than observed. Interestingly, the  $\text{NH}_3/\text{PH}_3$  abundance ratio in IRC +10216 ( $\sim 200$ ; Hasegawa et al. 2006) is similar to the solar elemental N/P abundance ratio, indicating that a similar fraction of N and P are locked in  $\text{NH}_3$  and  $\text{PH}_3$ , respectively. A non equilibrium chemistry driven by shocks induced by the stellar pulsation has been proposed as a source of water vapour in IRC +10216 (Cherchneff 2011). In this scenario, however,  $\text{NH}_3$  is formed with a very low abundance and details on whether or not  $\text{PH}_3$  is formed are not provided. Another mechanism proposed for the formation of hydrides such as  $\text{H}_2\text{O}$  and  $\text{NH}_3$  in the inner layers of carbon-rich envelopes such as IRC +10216 is photochemistry driven by the penetration of interstellar UV photons across the clumpy envelope (Decin et al. 2010; Agúndez et al. 2010). In this scenario  $\text{PH}_3$  is not efficiently formed although it is likely due to the lack of relevant chemical kinetics data for phosphorus species. Another possible source of hydrides such as  $\text{PH}_3$ , yet to be explored, could be provided by chemical reactions taking place on dust grain surfaces. Which of these mechanisms, if any, is responsible for the formation of  $\text{PH}_3$  in the ejecta of evolved stars such as IRC +10216

has yet to be investigated.

#### 4. SUMMARY

We use the HIFI instrument on board *Herschel* to observe the  $J = 2 - 1$  line of  $\text{PH}_3$  in IRC +10216, which together with the previous observation of the  $J = 1 - 0$  line with the IRAM 30-m telescope, definitively confirms the first identification of  $\text{PH}_3$  outside the solar system. Excitation and radiative transfer calculations indicate that the observed lines are consistent with phosphine being formed in the circumstellar envelope anywhere between 1 and  $100 R_*$  from the star with an abundance of  $10^{-8}$  relative to  $\text{H}_2$ . The detection of  $\text{PH}_3$  challenges chemical models as no obvious formation route has for the moment been found. Prospects to put further constraints on the distribution and origin of  $\text{PH}_3$  in IRC +10216 with telescope facilities such as ALMA seem challenging. The  $J = 1 - 0$  line being blended with a SiS  $v = 4$  line, it makes complicated to disentangle the contribution from each line to the spatial distribution of the emission. The  $J = 2 - 1$  line at 533.8 GHz cannot be reached from ground because of the terrestrial atmospheric opacity, and the  $J = 3 - 2$  line is also severely blended with a strong line of  $\text{SiC}_2$ . Although  $\text{PH}_3$  locks a minor fraction of phosphorus in IRC +10216, it is together with HCP, one of the major gas phase carriers of phosphorus in the inner circumstellar layers, suggesting that it could be also an important phosphorus species in other astronomical environments. Observations of  $\text{PH}_3$  in sources other than IRC +10216, such as CRL 2688, may help to better understand its formation and the implications for the chemistry of phosphorus in space.

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